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USE OF UNCONVENTIONAL INITIAL MATERIALS TO OBTAIN HEAT-PROOF CERAMIC

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It is shown that unconventional initial materials can be used to produce heat-proof cordierite-containing ceramics. Cordierite-containing articles with operating temperatures ranging from 1300 and 1100°C have been obtained on the basis of high- and low-melting Belarus clays.

Key words: cordierite ceramic, heat-resistance, phase composition, unconventional clayey initial materials

The adoption of new technologies and the advancement of engineering and practical use of different heating units in industry have made it necessary to use a wide spectrum of ceramic materials capable of withstanding sharp temperature differences.

Cordierite-based ceramic — magnesium aluminum silicate with the stoichiometric formula $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ — plays an important role in a number of heat-proof materials. Despite well-known drawbacks — relatively high synthesis temperature (> 1350°C) and narrow sintering interval (15 – 30°C), cordierite ceramic possesses a number of valuable properties — low CLTE, high resistance to corrosive agents, and adequate electric resistance and mechanical strength. These are the properties that are responsible for the wide use of this material in heat-proof components of heaters, IR emitters, lining of chemical reactors, hearths, filters, and other applications [1 – 5].

The statistical data show that about 70% of cordierite-based articles operate at temperatures not exceeding 1100 – 1150°C. Therefore it is logical for consumers to strive to lower their costs by using less expensive materials whose technical – operational properties may be limited but are nonetheless adequate in concrete cases.

In the Republic of Belarus there is a demand for cordierite-based articles with working temperatures not exceeding 1150°C. Research in this direction is being conducted at Belarus State Technical University. For example, it has been shown that the raw materials base for obtaining cordierite-containing ceramics can be expanded, and the raw materials available in Belarus can be brought into production.

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Specifically, conventional technology has been used to synthesize materials based on kaolinite hydromica clay from the Novoraiskoe deposit, gibbsite $Al(OH_3)$, and talc from the Onostskoe talc mine. Damaged articles were introduced into the mixes as grog addition, whose finely comminuted grains are uniformly distributed over the volume of the article; they also act as centers of crystallization of the main crystalline phase — cordierite.

The use of aluminum hydroxide is justified by its high reactivity (which is due to the dispersity of the material), its polymorphism on heating, and the influence of the water of crystallization, which, being released during heat treatment, intensifies the phase formation processes (so-called Hedval effect) that occur during synthesis.

High- and low-melting clays from the "Gorodnoe," "Gorodok," "Turovskoe," and "Gaidukovka" deposits were also used. A commercial composition based on kaolin, alumina, and talc was used for comparison. The chemical compositions of the raw materials are presented in Table 1.

Samples based on experimental mixes with stoichiometric composition close to cordierite were obtained by semidry pressing from powders which were comminuted beforehand in a vibrating mill to specific surface area about 13000 cm^2/g and pressed in hydraulic presses under pressure 35 MPa. Next the samples were dried and fired in the temperature range 1000 – 1350°C with temperature increasing at the rate 550 K/h and soaked at the maximum temperature for 1 h. The structure of the materials synthesized, using different initial clay materials as a base, during a single firing at 1250°C are presented in Fig. 1.

The results of optical microscopy show that the materials possess cryptocrystalline structure with glassy phase content no greater than 10 – 15%.

TABLE 1.

Material	Content, wt.%								
	SiO_2	Al_2O_3	$FeO + Fe_2O_3$	CaO	MgO	K_2O	Na_2O	TiO_2	calcination losses
Glukhovetskoe kaolin	49.89	40.60	0.45	–	–	0.15	0.05	–	8.85
DN-0 clay*	53.11	30.95	1.09	1.93	0.55	1.76	–	1.33	9.20
Onotskoe talc**	60.45	0.68	0.86	0.13	30.04	–	–	0.06	7.67
Gibbsite	0.19	62.50	0.01	–	–	1.00	–	–	36.31
Clay from the deposit:									
“Gaidukovka”	56.08	13.85	4.51	8.19	2.63	3.76	0.84	–	10.14
“Gorodnoe”	66.96	16.01	7.21	0.71	0.40	0.08	0.49	0.51	7.63
“Gorodok”	68.64	15.66	3.89	0.74	0.60	2.02	0.97	0.05	7.42
“Turovskoe”	69.04	14.96	3.38	1.08	0.39	0.57	0.23	0.77	9.59
Diaphorite	43.19	3.45	13.79	4.88	26.35	0.12	0.35	0.17	7.69
Dolomite	3.60	1.65	0.31	30.42	21.10	–	–	–	42.92

* The DN-0 clay also contained 0.08% P_2O_5.

** Onotskoe talc also contained 0.10% MnO.

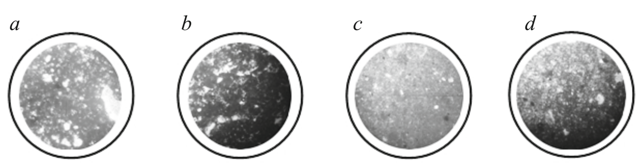

Fig. 1. Structure of ceramic materials (× 90) synthesized at 1250°C: based on kaolin (*a*), DN-0 kaolin hydromica clay (*b*), “Turovskoe” refractory clay (*c*), and “Gaidukovka” low-melting clay (*d*).

The chemical composition of the glassy phase, as determined with a JSM-5610 LV scanning electron microscope with an EDX JEC-2201 JEOL (Japan) chemical analysis system, of samples synthesized using DN-0 clay is as follows (wt.%): 6.833 CaO, 12.500 Al_2O_3, 8.000 K_2O, and 72.667 SiO_2.

X-ray phase analysis of the synthesized materials indicates a difference in their phase composition. The phase formation in the systems studied occurs by different mechanisms. Cristobalite is present in the compositions synthesized on the basis of kaolin in the temperature range 1150 – 1350°C; it is formed from amorphous silica, which precipitates in the course of the decomposition of kaolinite and vanished only after firing at high temperature (> 1350°C):

$$\underset{\text{metakaolinite}}{3(Al_2O_3 \cdot 2SiO_2)} \rightarrow \underset{\text{mullite}}{3Al_2O_3 \cdot 2SiO_2} + \underset{\text{amorphous silica}}{4SiO_2}.$$

In addition, cristobalite precipitates during high-temperature solid-phase reactions which ultimately result in the formation of cordierite.

The appearance of cristobalite in samples obtained using DN-0 clay as a base has also been recorded but only in a narrow temperature interval (1120 – 1170°C). When the calcination temperature is increased above 1170°C the cristobalite reflections vanish, evidently because of dissolution in the liquid phase.

It was determined that the presence of hydromica in the mixes promotes earlier formation (1000 – 1050°C) of viscous potassium-containing melt, whose presence retards the formation of cristobalite and completely suppresses it when the liquid phase content is high.

Cristobalite was not found in samples synthesized on the basis of high-melting clays from the “Turovskoe,” “Gorodnoe,” and “Gorodok” deposits and low-melting clay from the “Gaidukovka” deposit, but a spinel phase and free quartz, whose reflections are seen in the products of firing; these are formed in the reactions

$$\underset{\text{talc}}{3MgO \cdot 4SiO_3 \cdot H_2O} \rightarrow \underset{\text{enstatite}}{3(MgO \cdot SiO_2)} + \underset{\text{silica}}{SiO_2} + H_2O;$$

$$\underset{\text{enstatite}}{3(MgO \cdot SiO_2)} + \underset{\text{mullite}}{3Al_2O_3 \cdot 2SiO_2} \rightarrow$$
$$\rightarrow \underset{\text{spinel}}{3(MgO \cdot Al_2O_3)} + \underset{\text{silica}}{5SiO_2}.$$

In the case where clay from the “Gaidukovka” deposit is used, the substantial amount of a liquid phase, which already forms at 1000°C and results in the dissolution of the precipitated amorphous silicon in the melt, impedes the formation of cristobalite.

Interestingly, for cordierite ceramic obtained using kaolinite hydromica clay from the “Turovskoe” deposit, which clay is characterized by a low content of alkali oxides and hence low liquid-phase content and, conversely, a high free-quartz content, the precipitation of cristobalite is also

not observed but for a different reason. The amorphous silica precipitating during the decomposition of clayey material during calcination transforms into quartz, evidently as a result of the influence of impurities in the clay, which suppress the crystallization of cristobalite.

However, a substantial amount of free quartz in the "Turovksoe" clay impedes the formation of a sintered structure in the samples, as a result of which the product of firing is a conglomerate of weakly bound grains and possesses low mechanical strength.

As dilatometric investigations of ceramic samples show (Fig. 2), a peak is recorded in the curves of the CLTE versus firing temperature of the experimental mixes in the case where high-CLTE phases (mainly cristobalite) are formed. The intensity and region of existence of this peak depend on the type and chemical-mineral composition of the initial clay material.

We have made attempts to replace talc by other magnesium-bearing raw materials — dolomite from the "Ruba" deposit as well as diaphorite, containing complexes similar to the rocks on the Kola Peninsula and Central Urals. Their high content of magnesium oxide (26.0 – 26.5%) and iron oxide (12.5 – 13.8%) can be a favorable factor for the formation of a cordierite phase and for sintering of the materials.

However, it was determined that only part (up to 20 wt.%) of the talc can be replaced with dolomite or diaphorite. No considerable influence of the substitutions on the cordierite yield with decreasing cost of cordierite production was observed.

The investigations performed in [4, 5] show that the ceramic heat-proof materials synthesized on the basis of the refractory Belarus clays can be used up to temperature 1300°C and the materials based on the clay from the "Gaidukovka" deposit can be used up to 1100°C.

Seven hundred cordierite-containing articles (electric insulators for firing furnaces and chill casting machines), which have been in service for several years with no complaints, have been obtained on the basis of the proposed technology and are now used in manufacturing.

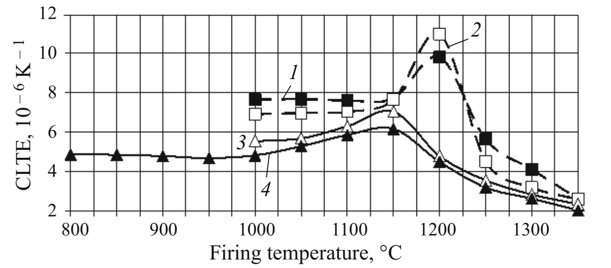

Fig. 2. CLTE of the samples versus the firing temperature: *1*) kaolin (clay); *2*) kaolin (gibbsite); *3*) DN-0 (clay); *4*) DN-0 (gibbsite).

In summary, it has been determined that unconventional raw materials can be used as a basis for producing heat-proof cordierite-containing ceramic.

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